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No. 321

THERMAL EXPANSION OF ALPHA AND OF BETA BRASS BETWEEN 0 AND 600° C, IN RELATION TO THE MECHANICAL PROPERTIES OF HETEROGENEOUS BRASSES OF THE MUNTZ METAL TYPE

BY

P. D. MERICA, Associate Physicist and L. W. SCHAD, Assistant Physicist Bureau of Standards

ISSUED MAY 9, 1918



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By P. D. Merica and L. W. Schad

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I. INTRODUCTION

In the course of recent investigation of the cracking or fracturing of brass articles of the type composition, 60 per cent copper and 40 per cent zinc, it has been possible to give adequate explanation for failure in most of the individual cases. These failures have been ascribed to excessive initial or service stress in conjunction with corrosion, or to the improper execution of the forging operation by which the article was formed. A number of instances of cracking in brass of this type have, however, come to the attention of the authors, for which these explanations can not be applicable. Such an instance is the following:

A 3/8-inch diameter naval brass hook bolt, which had been heated to "cherry red" and quenched in warm water, was used in the support of a strainer plate in a water-filter plant, under a tensile stress of from 10 000 to 15 000 pounds per square inch. After about 60 days it broke off, with practically no elongation. There was little initial stress in this bolt, and the load stress was not above the proportional limit; the subsequent cracking of the bolt appears, therefore, rather mysterious

Several naval brass rivets have been examined which had fractured at the shoulder, under a tensional stress no greater than that caused by the restrained thermal expansion of the rivet after heating.

These cases have been described more fully.1

In all of these instances, in which the usual mode of explanation of cracking has failed, it was discovered that the brass article

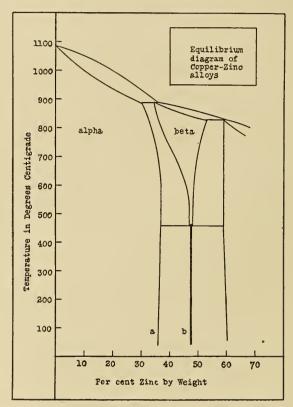


Fig. 1.—Portion of equilibrium diagram of copper-zinc alloys

had been subjected, at some time, to a very rapid cooling or quenching. Since the 60:40 (60 per cent copper and 40 per cent zinc) alloy is heterogeneous in structure, consisting of the two constituents, alpha and beta, in approximately equal proportions, the thought occurred to the authors that local stresses between the alpha and the beta constituents, caused by their unequal thermal expansion, might be developed during its rapid cooling. It was

¹ Merica and Woodward, Bureau of Standards, Technologic Paper No. 82, 1916; Trans. Am. Inst. Metals, 9, 298, 1915.

with the idea of obtaining some information on this point that the work described below was undertaken, with the purpose of determining the difference between the unit thermal expansion values of the two constituents, alpha and beta, of 60:40 brass.

Apparently there has been, hitherto, no investigation along this line, either with brass or with other heterogeneous alloys. Some determinations 2 have been made of the thermal expansion of brass of different compositions, particularly at ordinary temperatures.

It was desired in this work to compare the thermal expansion of alpha and beta brass 3 of compositions which are normally in equilibrium with each other at ordinary temperatures. In the case of the pure copper-zinc alloy, compositions such as those at a and b in Fig. 1 were chosen; in a slowly cooled alloy of any intermediate composition the concentrations of copper or zinc in the alpha and in the beta phases will be those given by these points. The preparation of homogeneous alloys of these compositions is not possible in general without appropriate heat treatment. The cast alpha brass must be annealed for some time at approximately 500° C and slowly cooled; the beta alloy may require to be quenched from above the transformation range and drawn to relieve stresses.

TABLE 1.—Composition of Brass Samples

N						
Number of alloy	Copper	Zinc	Tin	Lead	Iron	Phase
	Per cent					
215 a	65.6	32.9	1.3	0. 2	0.1	Alpha
216 a	54.5	43.9	1.3	.1	.2	Beta
250 a	53.5	45.6	.9	Trace	Trace	Alpha
252 a	54.7	44.5	.7	.1	.1	Do
256 a	65.3	34.5	. 23	. 2	Trace	Beta
257 a	67.2	32 0	.7	.1	.1	Do
259 b	64.6	35.4	.06	. 04	<.04	Alpha
261 b	55. 5	44.5	. 07	.05	≥.04	Beta

a These samples were east from some remelted copper and Horsehead spelter.

b These samples were cast from electrolytic copper and Horsehead spelter; they contained, therefore only slight amounts of impurities.

² Dittenberger, Zeit. Ver. deutsch. Ing., 16, p. 1532, 1902; Benoit, Journ. de Phys., 8, p. 471, 1889; Henning, Ann. d. phys., 22, p. 631, 1907; Price, Trans. Am. Int. Metals, X, p. 133, 1916.

3 Hereafter the terms "alpha" and "beta" will be used to denote the alpha and beta phases, respectively,

TABLE 2.—Heat Treatment of Alpha and Beta Alloys After Casting

Specimen	Time of heating	Temper- ature	Cooling	Time of heating	Temper- ature	Cooling	Time of heating	Temper- ature	Cooling
	Minutes	°C		Minutes	°C		Minutes	°C	
215A	10	700	f-c	60	600	f-c	180	600	t-c
216C	15	750	q-w	60	100-150	f-c	10	300-400	t-c
215C	10	700	f-c	60	600	f-c	180	600	f-c
250A	45	350-450	f-c						
250B	45	350-450	f-c						
252A	45	350-450	f-c						
252B	45	350-450	f-c						
256A	240	600	f-c						
256B	240	600	f-c						
257A	240	600	f-c						
257 B	240	600	f-c						
259 A	15	750	f-c						
261F	15	750	q-o	120	325	f-c			

f-c indicates furnace cooled.

q-w indicates quenching in water.

q-o indicates quenching in oil.

II. THERMAL EXPANSION OF ALPHA AND OF BETA BRASS

1. PREPARATION OF ALLOYS

The samples for the measurements were cast in chill molds, heat treated in order to produce a homogeneous, stress-free alloy, then machined and tested.

The specimens 259 and 261 were made of pure electrolytic copper and Horsehead zinc; the others were made of some remelted copper, together with Horsehead zinc and Straits tin. These samples, unfortunately, contained some lead and iron. The chemical analyses of the samples are given in Table 1.

After casting, the alpha brasses were annealed and the beta brasses treated as indicated in Table 2 in order to homogenize the alloy and relieve it of stress. The specimens were heat treated until they were homogeneous as determined microscopically; this required several periods of heating for some specimenas. An idea of the homogeneity of the alloys may be obtained from the micrographs, Figs. 6 to 11.

2. MEASUREMENT OF EXPANSION.

The thermal expansivity measurements were made in special apparatus designed and built at the Bureau of Standards for the purpose of obtaining good temperature uniformity and high accuracy in measuring length changes.

The specimens tested to 500° C or over were heated in air in an electric furnace in which the temperature as determined by differential thermoelements was uniform to 0.1° C throughout the entire chamber containing the specimen. The absolute tempera-

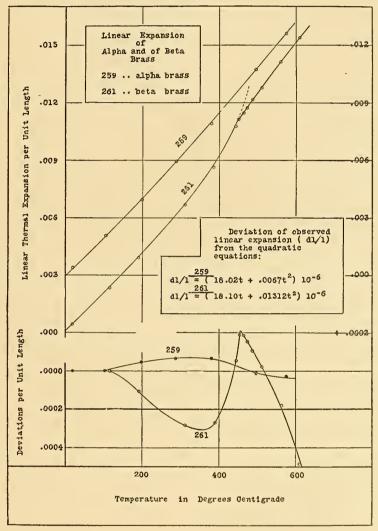


Fig. 2.—Expansion curves of brass

tures were determined by a carefully calibrated platinum platinum-rhodium thermoelement.

The tests to 300° or less were made in an oil bath in which the temperature variation was perhaps less than 0.1° C over the entire specimen. In this case the absolute temperatures were determined

with a copper-constantan thermoelement immersed in the oil at the side of the specimen.

The length changes were determined with a special comparator, consisting of two microscopes rigidly clamped on an invar bar at a

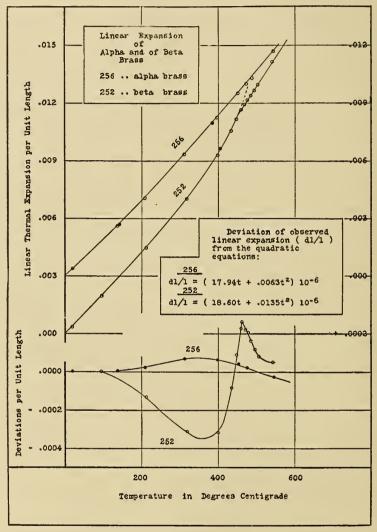


Fig. 3.—Expansion curves of brass

distance from each other equal to the length of the specimen and so arranged that they could first be sighted on a standard-length bar kept at a constant temperature and then on the 1 mil wires dropped over the ends of the specimen under test.⁴

⁴ Journal of the Washington Academy of Sciences, 11, p. 248; 1912.

The length changes measured in this way are accurate to about ± 0.001 mm, which on a specimen of 300 mm long (the standard length of the specimen) would be ± 0.0003 per cent.

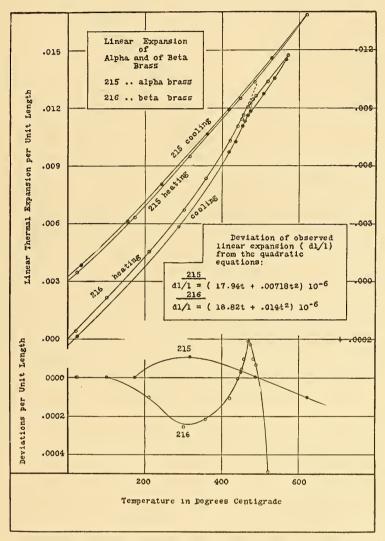


Fig. 4.—Expansion curves of brass: ○=points taken on heating; ●=points taken on cooling

For specimens heated in oil to 300° or less each test was completed in about five hours; the test to 600° C in the air furnace was completed in from three to five days. Experience seemed to show that the rapidity with which the test was made had little or no effect upon the behavior of the specimen.

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3. RESULTS AND DISCUSSION

The data are given in Figs. 2 to 5, in which is shown in each case the actual unit linear thermal expansion (linear expansion per unit length) and also the deviation of this observed expansion from that computed from a quadratic equation, which in each case best fits the series of observations.

The curves for alpha are continuous in each case up to 600° C, whereas the transformation of beta into beta prime is readily

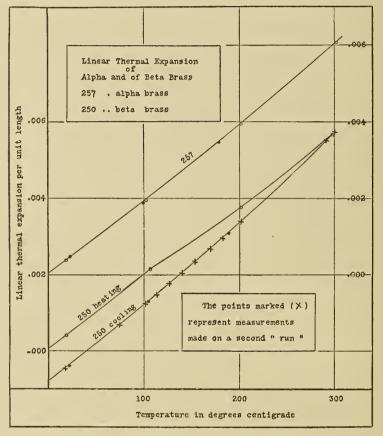


Fig. 5.—Expansion curves of brass

seen in the change in the slope of the beta curve at from 450 to 460° C. The first terms of the quadratic equation representing the thermal expansion are very nearly equal, although with a high tin content the value for beta becomes higher. The second term of the equation for alpha is, however, consistently lower than that of the beta; indeed, it is only approximately one-half of the second term of the beta equation. Thus, although from

o° to about 300° C the expansions of alpha and beta brass are almost equal, beyond this temperature and up to 460° C the expansion of the beta becomes almost twice that of the alpha. This is shown in Table 3. Above the transformation temperature the curve of the expansion of the beta is almost linear and runs nearly nearly parallel to that of the alpha.

The quadratic equations best fitting the observed expansions are given on the figures. It is to be noted:

- 1. That the portion of the beta curve up to 460° C would be better fitted with a cubic curve.
- 2. That above this transformation point the curve is approximately linear (to 600° C) and might be represented as follows:

TABLE 3.—Expansion	of Bra	s Over	Different	Temperature	Intervals
--------------------	--------	--------	-----------	-------------	-----------

Sasimon	Unit linear expansion per degree centigrade between—									
Specimen	20 and 100°	100 and 200°	200 and 300°	300 and 400°	400 and 450°	500 and 600°				
215A; alpha	19.2×10 ⁻⁶	20.0×10 ⁻⁶	22.0×10 ⁻⁶	22.5×10 ⁻⁶	23.5×10 ⁻⁶	24.5×10-6				
216C; beta	21.6×10^{-6} 20.1×10^{-6}	21.8×10-6	22.8×10 ⁻⁶	29.6×10-6	35.0×10 ⁻⁶	30.5×10-6				
252A; beta	22.8×10-6	19.4×10-6	23.5×10 ⁻⁶	27.5×10 ⁻⁶	39.2×10 ⁻⁶	26.9×10-6				
256A; alpha	18.7×10 ⁻⁶	20.0×10 ⁻⁶	22.0×10 ⁻⁶	22.5×10 ⁻⁶	23.0×10 ⁻⁶	23.7×10 ⁻⁶				
259A; alpha	22.8×10-6	22.2×10-6	21.9×10 ⁻⁶	22.2×10-6	23.4×10-6	23.6×10-6				
261 F ; beta	20.0×10 ⁻⁶	21.0×10-6	23.6×10−6	28.0×10 ⁻⁶	35.0×10 ⁻⁶	27.0×10-6				

For brass No. 261
$$\frac{dl}{l}$$
=26.5×10-6 t
For brass No. 252 $\frac{dl}{l}$ =27.9×10-6 t
For brass No. 216 $\frac{dl}{l}$ =25.2×10-6 t

The second term of a quadratic fitting these curves would be small (and negative in value for No. 261).

Very interesting are the deviations observed by subtracting the values computed from the quadratic equations noted in the curves (Figs. 2 to 5) from the observed expansions; these are plotted in the same figureon a larger scale. It is seen that the deviation of the alpha brass is at first zero, then at about 100 to 150° it becomes positive, attaining a maximum at from 300 to 350°, falling off thereafter to 0 at about 500° and becoming negative. The beta brass pursues almost the reverse course; the deviations attain a negative maximum at about 350°, rise to a sharp positive maximum at about 400°, and drop again rapidly. These deviations are quite regular and occur in all of the samples.

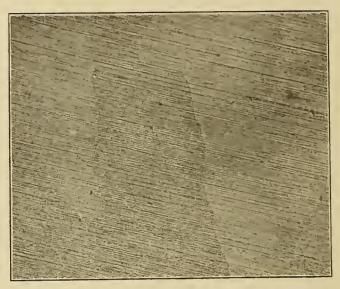


Fig. 6.—No. 215, alpha brass, cast and annealed. ×100



Fig. 7.—No. 216, beta brass, cast and annealed. ×100



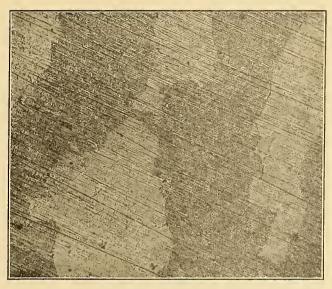


Fig. 8.—No. 256, alpha brass, cast and annealed. ×100

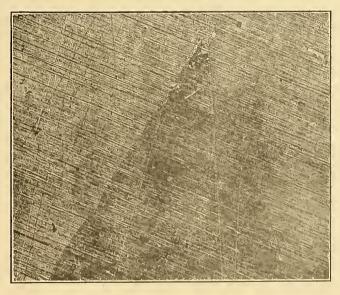


Fig. 9.—No. 252, beta brass, cast and annealed. ×100

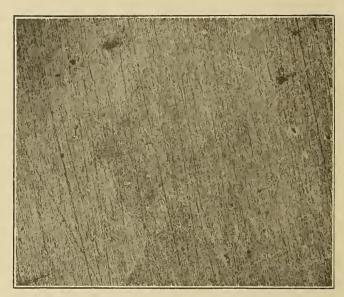


Fig. 10.—No. 259, alpha brass, cast and annealed. \times 100

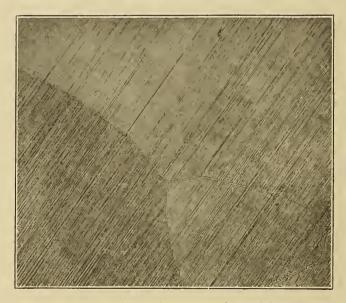


Fig. 11.—No. 261, beta brass, cast and annealed. ×100

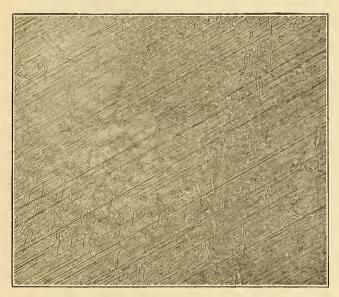


Fig. 12.—No. 261, beta brass, after heating to 600° C. ×100

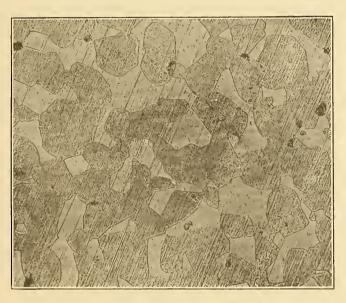


Fig. 13.—No. 169 Q, naval brass, quenched. ×500



Fig. 14.—No. 169 R, naval brass, quenched and drawn. \times 500

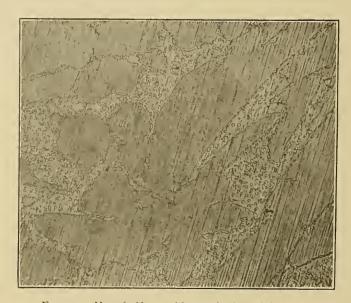


Fig. 15.—No. 169 V, naval brass, slowly cooled. ×500

They are related closely to the transformation point in the case of the beta brass.

In the case of the alpha brass a slight permanent elongation was noticed in some cases after heating to 600° C and cooling, whereas in the beta brass a shrinkage always took place. This shrinkage is most marked in specimen 250, Fig. 5, heated to 300° C; the corresponding alpha brass showed no change in length whatever. The second determination on the sample 250, indicated in Fig. 5, gave an expansion coinciding exactly with the "down" curve of the first.

It may be noted that some precipitation of alpha took place in the sample 261 upon heating between 400 and 600° C; this is shown in the micrograph, Fig. 12, showing the structure of the thermal expansion specimen after a 600° C heating.

This precipitation of alpha (which has a slightly different density than beta) would alter the observed coefficient through the temperature range of its precipitation.

Thus, if

V = specific volume of the alloy

 V_{α} = specific volume of the alpha constituent

 V_{β} = specific volume of the beta constituent

m =fraction of alpha by weight,

then
$$V = mV_{\alpha} + (1-m) V_{\beta}$$
.

$$\frac{dv}{dt} = m\,\frac{dV_\alpha}{dt} + V_\alpha\,\,\frac{dm}{dt} + (\mathbf{1} - m)\,\,\frac{dV_\beta}{dt} - V_\beta\,\frac{dm}{dt}$$

$$= \frac{dm}{dt} \ (V_{\alpha} - V_{\beta}) + m \ \left(\frac{dV_{\alpha}}{dt} - \frac{dV_{\beta}}{dt}\right) + \frac{dV_{\beta}}{dt}$$

Measurements showed the densities at ordinary temperatures of 259 (alpha) and 261 (beta) to be as follows:

$$259 \dots 8.294$$
 $V = \frac{1}{\text{density}}$

If it is assumed that 5 per cent of alpha has been formed between 460 and 480° C,

$$\frac{\Delta V}{\Delta T} = \frac{0.05}{20} \left(\frac{I}{8.294} - \frac{I}{8.226} \right) + \frac{dV_{\beta}}{dI} = -2.45 \times 10^{-6} + \frac{dV_{\beta}}{dl}$$

$$\therefore \frac{I}{L} \frac{dL}{L} = \frac{I}{3} \frac{dV}{dL} = (-0.82 + 26.5) \cdot 10^{-6}$$

The precipitation of alpha has therefore a small but appreciable effect on the thermal expansion coefficient.

4. LOCAL "GRAIN STRESSES" DUE TO DIFFERENCES IN THERMAL EXPANSION

It is much beyond the scope of this paper to attempt a discussion of the magnitude and distribution of stresses arising during the cooling of a heterogeneous aggregate of particles of different coefficients of thermal expansion. A particle imbedded in a homogeneous mass having a greater unit thermal expansion than it has, will be, after rapid cooling, essentially in hydrostatic or isotropic compression. The ground mass surrounding it will, at the surface of division, be subject to a system of tangential tensional stresses parallel to it. The magnitude and distribution of these stresses will depend on the size, shape of the imbedded particles and their distances apart.

One may gain a very rough idea of the magnitude of such stresses by assuming that the two constitutents are in the form of bars rigidly clamped parallel to each other. When the temperature of such a duplex bar is lowered there will be in each constitutent bar (if of equal cross section) a stress equal to

$$\frac{\Delta dL}{L} = \frac{E}{2}$$

where $\frac{\Delta dL}{L}$ = difference in thermal expansion per unit length between the constitutents.

E =modulus of elasticity.

Such stresses are calculated on the basis of E equal to 15 x 10 6 pounds per square inch and are given in Table 4. The values may be considered as representing the tensional stress in the beta and the compressional stress in the alpha bar which remain after cooling rapidly from the temperatures indicated. The reverse stresses would be temporarily caused by rapid heating. As the amount of beta in a brass is increased, the average stress from this cause in the beta would decrease; one would expect, therefore, other things being equal, to find a greater effect of such stresses in an alloy of beta than in one such as manganese bronze; a quenched alloy with alpha grains surrounded by beta envelopes should show most noticeably any effect of tensional stress in the beta constitutent.

It is noted that the development of stress, due to unequal thermal expansion, during the cooling of a 60:40 brass, is greatest within the temperature range from 300 to 500° C., at which experience has indicated, annealing and relief of stresses take place fairly readily. One may assume, therefore, that during slow cooling of such an alloy from 500 to 600°, the alloy constitutents yield locally under the stresses produced through the range 600 to 300°. Below 300° the contraction of the two constitutents is almost equal. During rapid cooling, however, the time may not be sufficient to allow of the local yielding to any extent of the constitutents; they arrive at ordinary temperature, therefore, in a state of stress described above.

TABLE 4.—Calculated Stresses Due to Difference in Thermal Expansion Between Alpha and Beta Brass

	For 215 and 216B	For 256 and 252B	For 259 and 261B
Difference in total unit linear expansion between 0° and 300°	0.00050	0.0005	0.00026
Corresponding stress pounds per square inch a	3750	3750	1950
Difference in total unit linear expansion between 0° to 400°	0.0012	0.0010	0.00075
Corresponding stress pounds per square inch a	9000	7500	5600
Difference in total unit linear expansion between 0° to 500°	0.0022	0.0021	0.00162
Corresponding stress pounds per square inch a	16 500	15 800	12 200
Difference in total unit linear expansion between 0° to 600°	0.0022		0.00190
Corresponding stress pounds per square inch a	16 500		14 200

^a Assuming two bars, one of A and one of B, rigidly clamped and heated from \circ° C to the temperature noted, or cooled through this range; E is assumed to be 15×10^{6} pounds per square inch.

III. EFFECTS OF CERTAIN HEAT TREATMENTS ON MECHANICAL PROPERTIES OF 60:40 BRASS

Some experiments were undertaken with a view to ascertaining directly whether the "grain" stresses described above exerted an appreciable effect upon the properties of the brass.

Six-inch lengths of drawn brass 1-inch diameter rods 164, 169, 171, 173, and 175 of the compositions and properties given in Table 5, were given the heat treatments described in Table 6, which consisted largely in the heating of the specimen to various temperatures between 400 and 600°C, and the quenching of them in water or oil. The samples were then submitted to the mercurous nitrate test. This test indicates the presence of initial stress of significant extent caused by drawing or working brass. None of the samples cracked during the quenching or in the test.

 $^{^6}$ Described more fully in Tables 2, 3, and 5 of Bureau of Standards Technologic Paper No. 82.

A few 1 inch diameter samples of naval brass and of Muntz metal were quenched or slowly cooled from 500° or from 400° C. These were then machined to 0.505-inch diameter and tested in tension. The results of these tests are shown in the Table 7. Without exception the quenched samples have a slightly lower proportional limit and a higher tensile strength than the samples which were slowly cooled from the same temperature or were quenched and drawn back to 400° C in order to relieve the local stresses.

It must be observed that the full effect of differential grain stresses on the mechanical properties of a brass might not be developed except when the brass was at the same time under additional tensional stress. The latter would increase the local tensional stresses and diminish the local compressional stresses such that an incipient local surface crack might develop throughout the brass. Information on this point could be obtained from the results of corrosion tests under stress such as are being conducted at present at the Bureau.

In the case of the naval brass the samples heated to 400° or thereabouts suffered in ductility, a fact which was readily explained by a miscroscopic examination of such samples. At that temperature the hard delta constitutent forms at the edge of the beta grains. This can be seen in the micrographs Figs. 13 to 15. At higher temperatures the quenched specimens did now show any delta.

TABLE 5.—Chemical Composition of Brasses Which Were Heat Treated and Tested in Tension

		•	Chemica	Physical properties			
Num- ber	Material		Zinc	Tin	Iron	Ultimate strength	Elonga- tion in 2 inches
		Per ct.	Per ct.	Per ct.	Per ct.	lbs./in.2	Per ct.
164	Muntz metal	61.1	38.5			72 000	a 16
169	Naval brass	61.2	37.5	1.2		83 000	13
171	Muntz metal	59.4	40.2			000 08	21
173	Manganese bronze	56.8	39.9	1.6	1.3	100 500	9
175	Manganese bronze	57.5	40.9	1.0	.6	77 000	27

a In 3 inches.

TABLE 6.—Heat Treatment of Brass Samples Submitted to Mercurous Nitrate Test

Specimen	Heat treatment
164A	1 hour at 430°, water quenched.
164B	1½ hours at 430°, oil quenched.
164C	1½ hours at 480°, water quenched.
164D	1½ hours at 480°, oil quenched.
169C	1½ hours at 480°, water quenched 750°-830°, water quenched.
169D	1½ hours at 480°, oil quenched
169K	20 hours at 625°, water quenched.
169 L	Do.
169 M	Do.
169N	30 minutes at 620-600°, water quenched tested.
169O	annealed 1 hour at 330°.
169P	20 minutes at 625 to 500°, water quenched.
169 T	20 minutes at 400°, quenched.
169W	40 minutes at 400°, furnace cooled.
171 F	20 minutes at 500°, water quenched.
171G	20 minutes at 500°, 20 minutes at 440°, water quenched.
171K	20 minutes at 500°, 20 minutes at 440°, furnace cooled.
175A	30 minutes at 445°, water quenched.
175B	30 minutes at 440°, oil quenched.
171C	1½ hours at 480°, water quenched.

TABLE 7.-Mechanical Properties of Heat-Treated Naval Brass and Muntz Metal

		Physical properties						
Speci- men	Heat treatment	Ultimate strength	Proportional limit	Elastic modulus	Elonga- tion in 2 seconds	Reduc- tion of area		
		Lbs./in.2	Lhs./in.2	Lhs./in.2	Per cent	Per cent		
	(30 minutes at 600-620° tested	59.7×108	14.0x103	14.4×106	34.5.	33.0		
169Q	Followed by 20 minutes at 500°,							
	water quench, 1 hour at 330°	56.6	18.0	16.0	21.0	21.6		
169S	15 minutes at 428°, water quench	63. 2	16.5	14.3	26.5	25.0		
169 V	20 minutes at 428°, furnace cooled	61.6	20.0	14.8	30.0	25. 1		
171D	(20 minutes at 500°,) (2 seconds at	59. 3	16.2	13.9	53.0	57.1		
	{ water quench. } { 400°.							
171E	l tested	60.4	14.0	14.3	53. 0	57.6		
171H	20 minutes at 500° (water quench	58.8	12.5	13.7	54.0	58.6		
	Followed by {							
171 J	20 minutes at 440° (furnace cooled	57.7	16.2	13.9	54.5	59.1		

IV. CONCLUSION

The difference in the thermal expansion of alpha and of beta brass of compositions which normally are in equilibrium in such alloys as Muntz metal, naval brass, etc., has clearly been shown by the measurements made. Fundamental variations in behavior as regards thermal expansion at temperatures up to 600°C

were noted, due to the occurrence of a transformation in the beta constituent

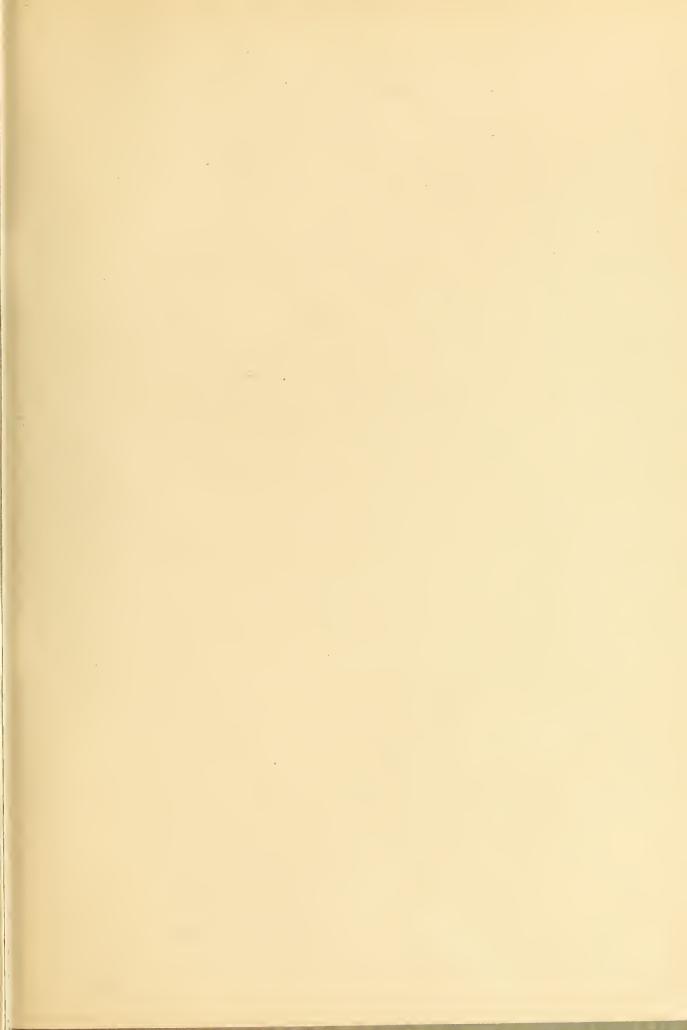
The effect of the local or, as they might be called, "grain" stresses, on the physical properties and service behavior has been only incompletely indicated. Tests showed that stresses of this sort produced by quenching commercial drawn 60:40 brass 1-inch diameter rod did not cause cracking in mercurous nitrate. On the other hand, a lowering of the proportional limit of the alloy amounting to about 2000 pounds per square inch resulted from this treatment.

Manufacturers of brass never quench 60:40 brasses; in fact, among them there seems to exist a disposition to regard this as dangerous practice. However, no definite data other than that recorded above are known to the authors, which would show clearly the ill effects of such sudden cooling.

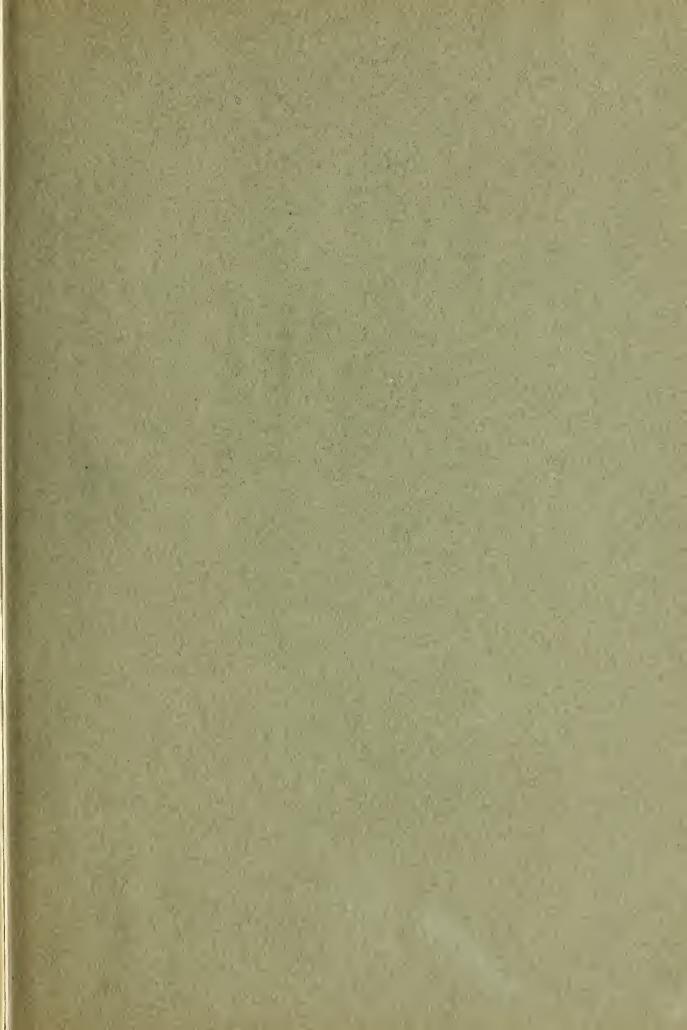
It is found that naval brass or manganese bronze when quenched in such a manner as to leave the beta grains surrounded by alpha envelopes, is generally both weak and brittle, and the fracture intercrystalline, a condition which has been ascribed to the alpha envelope. Now it is known that alpha brass is weaker than beta, but not more ductile, such that the authors suggest that as an explanation for this brittleness may more readily be assigned to existence of tangential tensional stresses in the beta grains immediately adjacent to the alpha envelope.

It would appear to the authors that further investigation into this general question of the expansion behavior of different constituents of other alloys might reveal causes of mysterious failures and weakness now considered quite obscure. Such materials as hypereutectoid steels, cast iron, type metal, and bearing metals contain two constituents. In many cases one of these constituents is brittle, a fact which would accentuate the effect of local contraction stresses. The authors hope to be able to present some data later along these lines, indicating also more definitely the physical effect of such stresses.

Washington, August 15, 1917.







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